Final Report

Improve thermoelectric efficiency of silicon nanowires

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14. ABSTRACT
In this project, we have focused on how to improve the thermoelectric properties of Silicon nanowires, in particular by using doping. We have studied two kinds of doping for Silicon nanowires (1) Silicon nanowire is doped with its isotope. We found that when 28Si nanowire is doped with 50% 29Si its figure of merit (ZT) can be enhanced by 31%. (2) Silicon nanowire is doped with Ge. Our study shows that when n-type Silicon nanowire is doped with 50% Ge, its ZT can be 4.3 times of that of Si nanowires. This means that if the ZT value of Si nanowire is about 0.6-1 as claimed by experiments, then the ZT value of n-type 0.5 0.5 Si Ge can be as high as 2.5-4.3. This makes Ge doped Si nanowire a promising candidate for industrial applications.

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1. Abstract

In this project, we have focused on how to improve the thermoelectric properties of Silion nanowires, in particular by using doping. We have studied two kinds of doping for Silicon nanowires:

(1) Silicon nanowire is doped with its isotope. We found that when ^{28}Si nanowire is doped with 50% ^{29}Si, its figure of merit (ZT) can be enhanced by 31%. The results have been published in Applied Physics Letter 95, 063102 (2009);

(2) Silicon nanowire is doped with Ge. Our study shows that when n-type Siliocon nanowire is doped with 50% Ge, its ZT can be 4.3 times of that of Si nanowires. This means that if the ZT value of Si nanowire is about 0.6-1 as claimed by experiments, then the ZT value of n-type $Si_{0.5}Ge_{0.5}$ can be as high as 2.5-4.3. This makes Ge doped Si nanowire a promising candidate for industrial applications. The results have been submitted to Applied Physics Letter for publication.

2. Objectives:

The objective of this proposal is to study the possible ways to improve ZT of semiconductor nanowires by reducing thermal conductivity from phonons. We will concentrate on the computational study of how isotope (impurity), quasi-periodic structure (interface) and the substrate reduce the thermal conductivity due to phonons thus increase the ZT of different semiconductor materials.

3. Introduction:

Thermoelectric material will play an important role in recycling the wasted heat. The efficiency of thermoelectric material is determined by the figure of merit: $ZT = \frac{S^2 \times \sigma}{\kappa} T$, here S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity. $\kappa = \kappa_e + \kappa_p$, where κ_e and κ_p are the electron and phonon (lattice vibration) contribution to the thermal conductivity, respectively. In order to make thermoelectric materials competitive, the ZT of the material must be larger than three. However, the road to achieve this goal has not been very smooth so far. First, simple increase S for general materials will lead to a simultaneous decrease in σ. Also, an increase in σ leads to a comparable increase in the electronic contribution to κ.

Nanostructured materials have been come to the spotlight in the last decade. It is expected to have larger ZT compared with the bulk counterpart. The possible underlying mechanism is that the density of states near the Fermi energy level is increased and the reduction in the thermal conductivity can be reduced significantly [1-4]. For example, Silicon nanowire (Si NW)'s thermal conductivity is found100 times smaller than that of bulk silicon [5-10] because of the rough surface scattering.

Moreover, our molecular dynamics (MD) modelling demonstrate that isotopic doping provides an effective approach to decrease thermal conductivity of carbon nanotube by 50% [11], this theoretical prediction has been confirmed experimentally by Berkeley's group [12]. Therefore, we can also apply the same strategy to reduce further the NW's thermal conductivity. Indeed, in our recent simulation [13], we found that the thermal conductivity can be tuned by the Ge contents thus open the door for increasing the ZT further. Indeed, it has been observed experimentally that when the Ge content in $Si_{1-x}Ge_x$ nanocomposites increases from 5% to 20%, the thermal conductivity decreases obviously. [14] However, at the same time, the power factor also decreases, and induces uncertainty in the change of figure of merit ZT. Although a number of studies have been reported recently about the thermal and thermoelectric

properties of $Si_{1-x}Ge_x$ nanocomposites and nanowire[13-20], it is still not clear on the quantitative impact of the composition on the thermoelectric performance.

In this project, we would like to investigate the doping effect Germanium to Silicon nanowire. Since the big difference of the Germanium atoms from Silicon atoms, we should expect a large reduction of thermal conductivity of Siliocn nanowire more than 50%, thus can double the ZT of silicon nanowire. More precisely, we would like to calculate the doing effect on all relevant physical quantities like Seebeck coefficient, thermal power, the electrical conductivity and thermal conductivity due to both electrons and phonons, and eventually ZT. With computer simulation, we expect better understand of the underlying physics thus we shall be able to work out a recipe for the design of the silicon nanowire for the thermoelectric application.

4. Theory and Computational methods

The electrical conductivity σ, the thermal conductivity due to electrons κ_e, and the Seebeck coefficient *S*, are obtained from the electronic structure with the solution of 1-Dimensional Boltzmann transport equation as:

$$\begin{aligned}
&\sigma = \Lambda^{(0)} \\
&\kappa_e = \frac{1}{e^2 T}[\Lambda^{(2)} - \Lambda^{(1)}(\Lambda^{(0)})^{-1}\Lambda^{(1)}] \\
&S = \frac{1}{eT}(\Lambda^{(0)})^{-1}\Lambda^{(1)} \\
&A^{(n)} = e^2\tau\frac{2}{m^*}\sum_{E_k}\Delta E\left[\frac{\beta\exp(\beta(E_k-\mu))}{(1+\exp(\beta(E_k-\mu)))^2}\right]D(E_k)E_k(E_k-\mu)^n
\end{aligned} \qquad (1)$$

Here *e* is the charge of carriers, *T* is the temperature, E_k is the electron energy, τ is the relaxation time, m* is the effective mass of the charge carrier, μ is the electron chemical potential and $D(E_k)$ is the density of states. The relaxation time τ, is a complex function of the electronic structure, temperature and carrier concentrations. The purpose of our work is to determine the qualitative effect of SiNW's transverse dimension on its thermoelectric property. In this work, we obtain the value of relaxation time by fitting the calculated mobility to measured electrical conductivity data of SiNW.

As the lack of experimental electrical conductivity data on diameter dependence, here we use the experimental data of SiNW with fixed diameter of 48 nm (n=1.7×10^{19} cm^{-3}, σ=588 $(\Omega cm)^{-1}$, from Ref. [5], and obtain $\tau = 4.3\times10^{-16}$ s for n=1.7×10^{19} cm^{-3}. Then, we use the dependence relation between the mobility and carrier concentration in bulk silicon in Ref. [21] to calculate the carrier concentration dependent relaxation time. For example, $\tau = 1.7\times10^{-15}$ s for n=1.0×10^{17} cm^{-3}, and $\tau = 9.7\times10^{-16}$ for n=5.0×10^{17} cm^{-3}. As *ZT* of n-doped SiNWs is considerably larger than that of their p-doped counterparts, we only study n-doped wires. The carrier concentration is defined as: $n = \int D(E-\mu)\times f(E-\mu)\times dE$, where *f(E)* is the Fermi distribution function.

For $Si_{1-x}Ge_x$ NWs we focus on that NWs oriented along the [110] direction with rectangular cross section area of 2.3 nm^2. The atomic structure is initially constructed from diamond structured bulk silicon. Then Si atoms are randomly substituted by Ge atoms and the geometry is relaxed to its closest minimum total energy. The surface dangling bonds are terminated with hydrogen atoms. A supercell approach is adopted where each wire is periodically repeated along the growth direction. The size of the supercells in the transverse plane is large enough (>15 Å from surface to surface). In this letter, the density functional

theory (DFT) calculations are carried out by DMol^3 package [22]. The DFT calculations are performed by using generalized gradient approximation (GGA) with the functional parameterized by Perdew, Burke, and Enzerhof (PBE) [22]. And the double-numerical-polarization (DNP) basis set is employed. Self-consistent field calculations are done with a convergence criterion of 10^{-6} hartree on the total energy. The Brillouin zone integration is performed using a 6×6×6 Monkhorst-Pack *k*-point grid. All the structures are fully optimized with a convergence criterion of 0.002 hartree/Å for the forces and 0.005 Å for the displacement. A real-space cutoff of 4.0 Å for the atom-centered basis set is chosen to increase computational efficiency while not significantly affecting the magnitude of inter-atomic forces or the total energies. The Gaussian smearing of electron density is applied with the energy range of 0.1 eV.

The electrical conductivity σ, the thermal conductivity due to electrons κ_e, and the Seebeck coefficient *S*, are obtained from the electronic structure with the solution of 1-Dimensional Boltzmann transport equation as mentioned above. Here we use the experimental data of n-type $Si_{0.95}Ge_{0.05}$ alloy ($n = 1.5\times10^{20} cm^{-3}, \sigma = 3400(Scm^{-1})$ from Ref. [14], and the dependence relation [19] between the mobility and carrier concentration in $Si_{1-x}Ge_x$ alloys to calculate the carrier concentration dependent relaxation time.

References:

[1] L. D. Hicks and M. S. Dresslhaus, Phys. Rev. B **47**, 16631 (1993).
[2] R. Venkatasubramanian, E. Siivola, T. Colpitts, and B. O'Quinn, Nature **41**3, 597 (2001).
[3] T. C. Harman, P. J. Taylor, M. P. Walsh, and B. E. LaForge, Science **30**3, 818 (2004).
[4] Y. Ma, Q. Hao, B. Poudel, Y. C. Lan, B. Yu, D. Z. Wang, G. Chen, and Z. F. Ren, Nano. Lett. **8**, 2580(2008).
[5] A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar, and P. Yang, Nature **451**, 163 (2008).
[6] A. I. Boukai, Y. Bunimovich, J. T. Kheli, J-K Yu, W. A. Goddard III, and J. R. Heath, Nature **451**, 168 (2008).
[7] T. Vo, A. J. Williamson, V. Lordi, and G. Galli, Nano Lett. **8**, 1111 (2008).
[8] L. H. Shi, D. L. Yao, G. Zhang, and B. Li, Appl. Phys. Lett. **95**, 063102 (2009).
[9] G. Zhang, Q. X. Zhang, C. T. Bui, G. Q. Lo, and B. Li, Appl. Phys. Lett., **94**, 213108 (2009).
[10] N. Yang, G. Zhang, and B. Li, Nano Lett. **8**, 276 (2008).
[11] G. Zhang and B Li, J. Chem. Phys **123**, 114714 (2005)
[12] C.-W Chang, D. Okawa, H. Garcia, A. Majumdar, and A Zettl, Phys. Rev. Lett **101**, 075903 (2006).
[13] J. Chen, G. Zhang, and B. Li, Appl. Phys. Lett. **95**, 073117 (2009).
[14] G. H. Zhu, H. Lee, Y.C. Lan, X.W. Wang, G. Joshi, D.Z. Wang, J. Yang, D. Vashaee, H. Guilbert, A. Pillitteri, M.S. Dresselhaus, G. Chen, nad Z.F. Ren, Phys. Rev. Lett. **102**, 196803(2009).
[15] X.W. Wang, H. Lee, Y.C. lan, G.H. Zhu, G. Joshi, D. Z. Wang, J. Yang, A.J. Muto, M.Y. Tang, J. Klatsky, S. Song, M.S. Dresselhaus, G. Chen, and Z.F. Ren, Appl. Phys. Lett. **93,** 193121(2008).
[16] G. Joshi, H. Lee, Y.C. Lan, X.W. Wang, G.H. Zhu, D.Z. Wang, R. W. Gould, D. C. Cuff, M.Y. Tang, M.S. Dresselhaus, G. Chen, and Z.F. Ren, Nano. Lett. **8**, 4670-4674, (2008).
[17] J. P. Dismukes, L. Ekstrom, E.F. Steigmeier, I. Eudman, and D.S. Beers, J. Appl. Phys. 35, 2899 (1964).
[18] C. B. Vining, J. Appl. Phys. **69**, 331(1991).
[19] G. A. Slack and M. A. Hussain, J. Appl. Phys. **70**, 2694(1991).
[20] O Yamashita and N. Sadaromi, Jpn. J. Appl. Phys. **38**, 6394-6400 (1999).
[21] C. Jacoboni, C. Canali, G. Ottaviani, and A. A. Quaranta, Solid-State Electronics, **20**, 77, (1977).
[22] DMOL is a density functional theory package distributed by Accelrys Inc; B. Delley, J. Chem. Phys., **92**, 508 (1990).
[23] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett., **77**, 3865, (1996).

5. Results and discussions

5.1 Thermal electric properties of isotope doped silicon nanowires

In this part we present our results on size dependence of physical properties of Si NW.

Fig. 1(a) and (b) show the size effect on σ and *S* with different electron concentration. σ increases slightly as the diameter increases, while the Seebeck coefficient *S* decreases remarkably. The size dependence arises from quantum confinement effect on the electronic band structure.

Figure 1(c) and (d) show that *S* decreases as the carrier concentration increases, while σ increases as more carriers are available to transport charge. Detailed discussions can be found in our publication in APL (2009).

The power factor *P* ($P = S^2\sigma$), is an important factor influencing the thermoelectric performance directly. Figure 2 (a) shows the power factor versus carrier concentration there is an optimal carrier concentration N_{Max} yielding the maximum attainable value of P_{Max}

The figure of merit, *ZT* is another important thermoelectric characteristic. In the calculation of *ZT*, both electron and phonon contribute to the total thermal conductivity. Figure 3(a) shows the dependence of electron thermal conductivity on carrier concentration for different transverse size. It is clear that electron thermal conductivity increases with carrier concentration as it is proportional to electronic conductivity, and SiNW with larger diameter is with higher electron thermal conductivity. For SiNWs with length in μm scale, the phonon thermal conductivity increases with diameter increases remarkably until the diameter is larger than about hundreds nms.

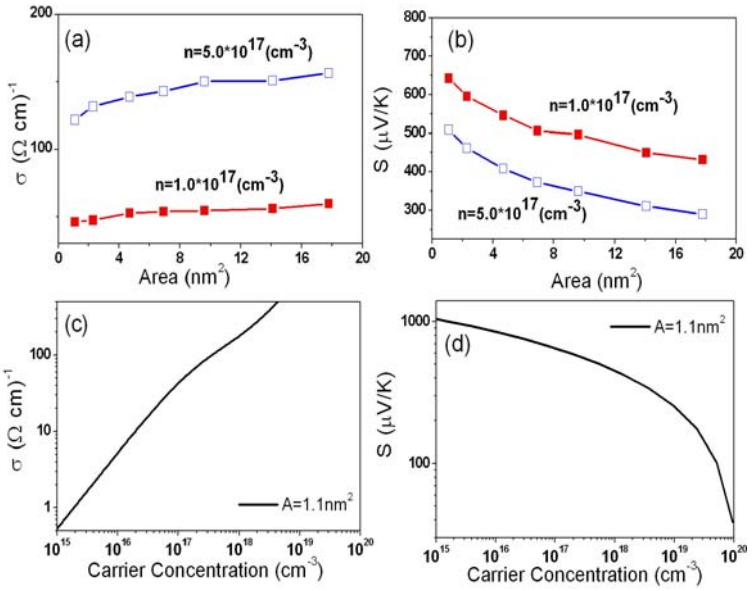

Figure 1. (a) Electrical conductivity vs cross sectional area with different carrier concentration. (b) *S* vs cross sectional area with different carrier concentration. (c) Electrical conductivity vs carrier concentration with fixed cross section area of 1.1 nm^2. (d) *S* vs carrier concentration with fixed cross section area of 1.1 nm^2.

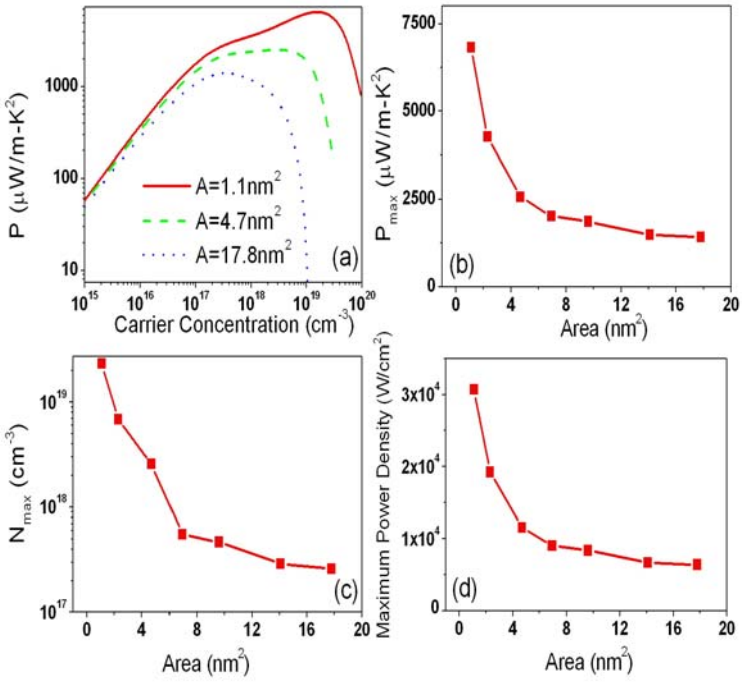

Figure 2. (a) Thermal power factor of SiNW vs carrier concentration with three different transverse dimensions. (b) Maximum power factor vs cross sectional area. (c) N_{Max} vs cross sectional area. (d) Size dependence of the maximum room temperature cooling power density of SiNW with length of 1μm.

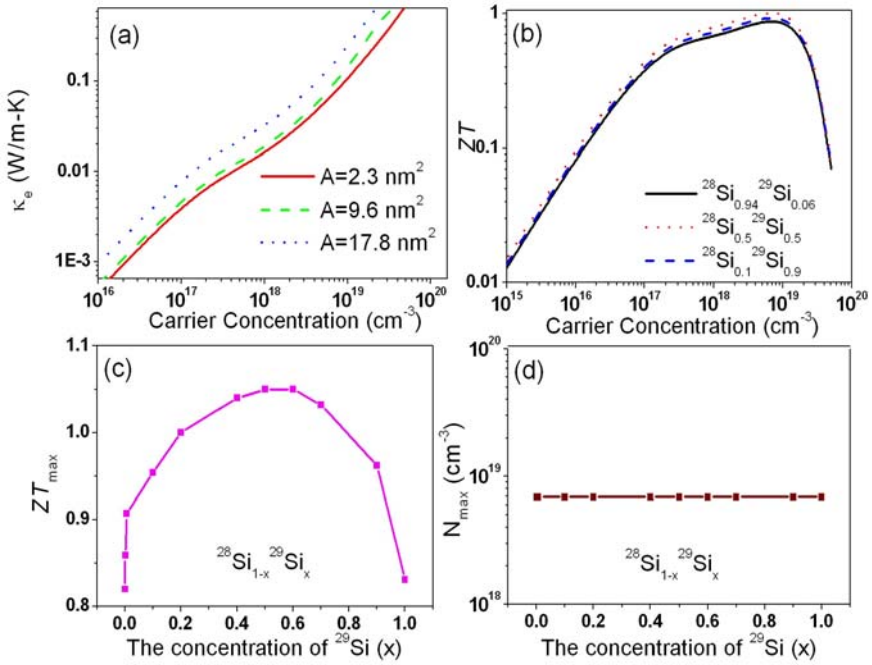

Figure 3. (a) Thermal conductivity due to electrons vs carrier concentration for SiNWs with different transverse dimensions. (b) *ZT* vs carrier concentration for different isotope-doped SiNWs ($^{28}Si_{1-x}{}^{29}Si_x$ NWs) with fixed cross section area of 2.3 nm^2. (c) ZT_{Max} vs the concentration of ^{29}Si atom. (d) N_{Max} vs the concentration of ^{29}Si doping atom

5.2 Thermal electric properties of Ge doped silicon nanowires

In Figure 4(a)-(d) we show the Ge content dependence of σ and *S* with different electron concentration for $Si_{1-x}Ge_x$ NWs. Here we choose the heavily doped case because the maximum *ZT* is expected to occur for high carrier concentration, which has been confirmed experimentally, and also to reduce the unknown effects of the band-gap uncertainty on the calculated values of *S.*

Figure 5 (a) and Figure 5(b) show the power factor *P* ($P = S^2 \times \sigma$) versus carrier concentration for n-type and p-type wires. There is an optimal carrier concentration N_{Max} yielding the maximum attainable value of P_{Max}. Here, N_{Max} is around $n = 2.0 \times 10^{20} cm^{-3}$ for n-type wires and $n = 1.0 \times 10^{21} cm^{-3}$ for p-type wires. As the Ge content increases, for n-type wires, P_{Max} decreases remarkably until x=0.5, and then increases with x as shown in Figure 5(c). For p-type wires, P_{Max} decreases (Figure 5(d)) with the Ge content increases monotonically until $x = 0.8$. The large fluctuation is partially due to the effects of the band-gap uncertainty on the calculated values.

The most significant results in the current work are shown in Figure 6. Here we focus on the relative change of *ZT* in n-type $Si_{1-x}Ge_x$ NWs and compare it with pure Si NWs. Using our calculated power factor from Figure. 5, and the relative phonon thermal conductivity ($\kappa_{SiGe} / \kappa_{Si}$, here κ_{Si} and κ_{SiGe} are thermal conductivities of SiNW and $Si_{1-x}Ge_x$ NW, respectively) calculated by using molecular dynamics method from Ref. 11, the dependence of $ZT_{Si_{1-x}Ge_x} / ZT_{Si}$ on Ge content x is shown in figure 4. The $ZT_{Si_{1-x}Ge_x} / ZT_{Si}$ values increase with Ge content, reach a maximum and then decreases. At low Ge content, the small ratio of Ge atoms can induce large increase in *ZT*. For instance, in the case of

$Si_{0.8}Ge_{0.2}$ NW, namely, 20% Ge, $ZT_{Si_{1-x}Ge_x} / ZT_{Si}$ is about 3. And with 50% Ge atoms ($Si_{0.5}Ge_{0.5}$ NW), the $ZT_{Si_{1-x}Ge_x} / ZT_{Si}$ can be as high as 4.3. The similar dependence of *ZT* is also observed in p-type wire, although its *ZT* is much lower than that in n-type wire. This phenomenon can be understood as the following. *ZT* is contributed by both power factor and thermal conductivity.

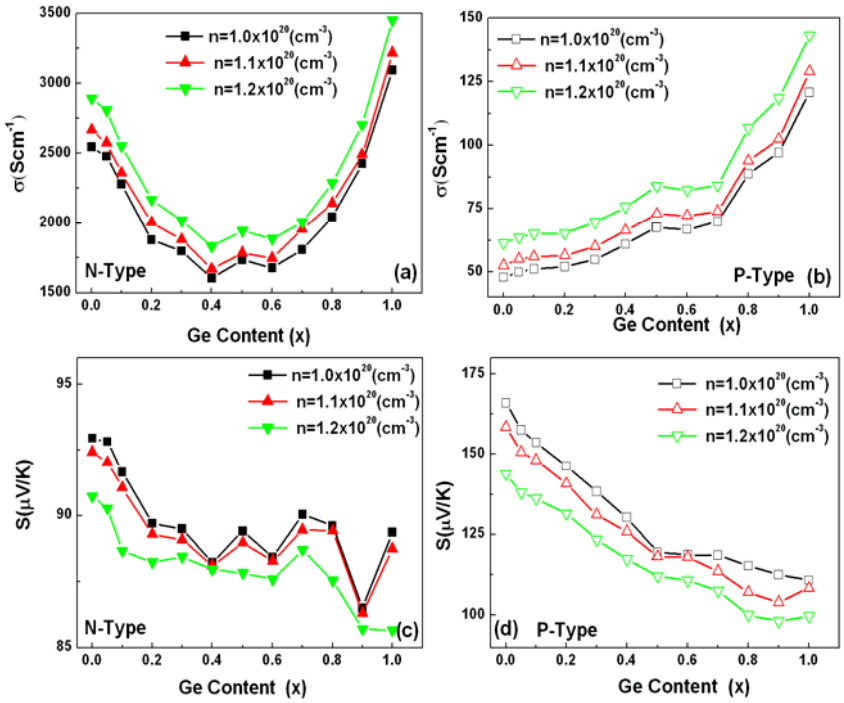

Figure 4. σ vs Ge content x with different carrier concentration for n-type wires (a) and p-type wires (b). *S* vs Ge content with different carrier concentration for n-type wires (c) and p-type wires (d).

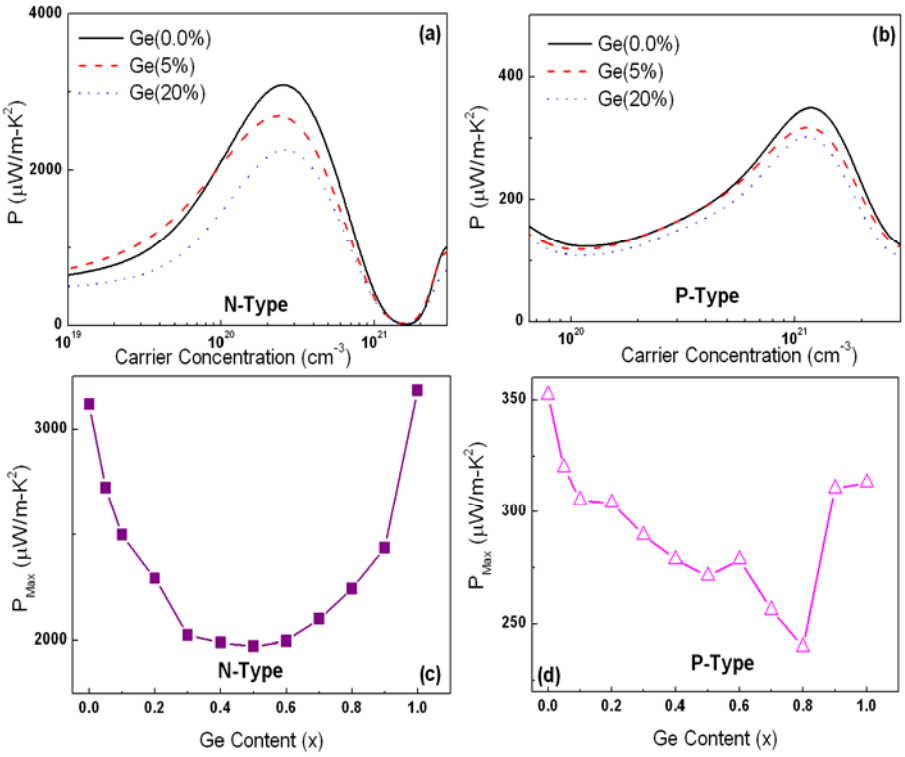

Figure 5. Thermal power factors of $Si_{1-x}Ge_x$ NWs versus carrier concentration with three different Ge contents for n-type wires (a) and p-type wires (b). Maximum power factors versus Ge content for n-type wires (c) and p-type wires (d).

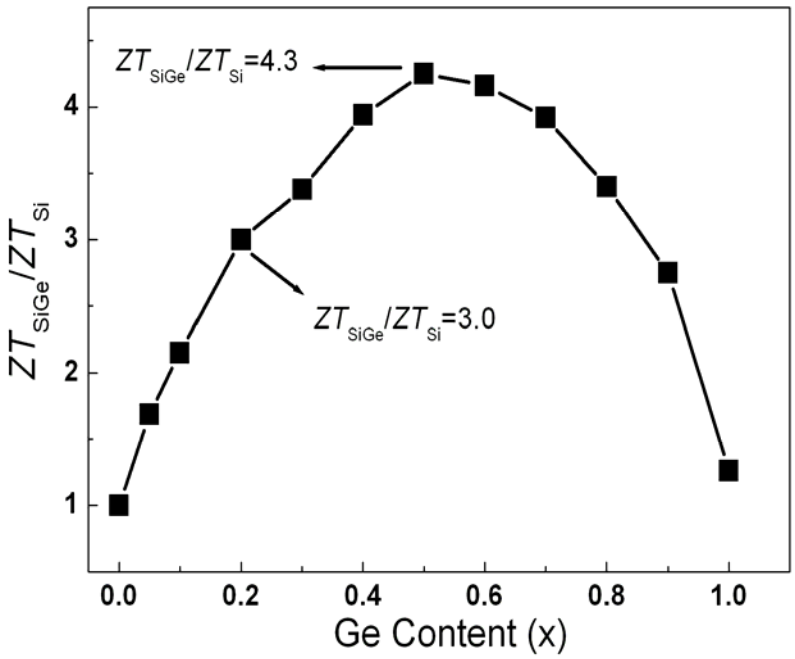

Figure 6. $ZT_{Si_{1-x}Ge_x} / ZT_{Si}$ versus the Ge content x for n-type $Si_{1-x}Ge_x$ wires.

6. Personal involved in the project

Miss Shi Lihong, a research assistant has been the main man power in this project.
Mr. Yao Donglai, another research assistant has also been involved partially in the project.

7. Publication List

Two papers have been resulted from this project.

7.1 L-H Shi, D.-L Yao, G. Zhang, and B. Li, Size-dependent thermoelectric properties of silicon nanowire, Applied Physics Letters, 95, 063102 (2009), published on 10 August 2009.

7.2 L.-H Shi, D.-L Yao, G. Zhang, and B. Li, Large Thermoelectric Figure of Merit In $Si_{1-x}Ge_x$ Nanowires, Applied Physics Letters, (submitted for publication in Nov 2009)